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ULTRA-HIGH-RESOLUTION FLUORESCENCE SPECTROSCOPY UPON EXCITATION OF ATOMS BY PULSED RADIATION IN THIN GAS CELLS

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The method of sub-Doppler fluorescence spectroscopy is proposed and is based on the narrowing behavior with time of the velocity distribution of optically excited atoms (molecules) of a rarefied gas medium in a thin cell after exposure to a sufficiently short light pulse. Changes in the established sub-Doppler resonances with time and the essential dependence of these resonances on the gas-cell dimensions are analyzed.

Keywords: *sub-Doppler fluorescence resonances, thin gas cell, short light pulse, spontaneous transitions.*

Introduction. Effective methods allowing the structure of spectral lines and masked Doppler broadening to be analyzed must be developed for ultra-high-resolution spectroscopy [1]. The progress and potential of well-tested sub-Doppler spectroscopy based on transient relaxation and optical pumping of atoms in thin gas cells with thicknesses many times less than their characteristic transverse dimensions have been reviewed [2]. For example, sub-Doppler resonances in absorption spectra in such gas cells was detected by monochromatic laser radiation scanned over frequency. New narrow sub-Doppler resonances were found and analyzed based on theoretical calculations directly in the fluorescence of atoms (molecules) in thin gas cells upon their irradiation by steady-state broadband radiation [3]. The present work showed that the use of pulsed radiation to pump atoms (molecules) in such cells opened new possibilities for ultra-high-resolution fluorescence spectroscopy. Narrow sub-Doppler resonances that could be recorded in the fluorescence of a thin gas layer after irradiation by a sufficiently short exciting pulse were found and analyzed.

Basic Expressions. Let us examine a rarefied gas medium in a cell fabricated from a transparent material that is shaped as a rectangular parallelepiped (Fig. 1). The inner thickness l of the cell (along the z axis) is many times less than its characteristic transverse dimension d (along the x and y axes). The gas medium in the cell is assumed to be rarefied enough that interaction of gas atoms in it can be neglected. This medium is irradiated in the interval $-T \le t \le 0$ by a sufficiently short broadband pump pulse that transitions atoms from the ground level a into excited state b. The population of excited level b after the action of this pulse decreases over time not only because of radiative decay (with characteristic time τ_b) but also because of collisions of the atoms with the cell walls. Thus, only those excited atoms whose velocity projection v_x, v_y, and v_z on the x, y, and z axes satisfy the below conditions can remain in the cell after time $t > 0$:

$$|v_x|\ t \le d,\ |v_y|\ t \le d,\ |v_z|\ t \le l\ . \tag{1}$$

The pulse length T is assumed to be short enough that the inequalities $T << \tau_b$ and $T << l/u$, where u is the most probable velocity of the gaseous atoms, are fulfilled. Then, both radiative relaxation of excited particles and the relative number of such particles that manage to collide with the cell walls according to Eq. (1) during the pulse can be neglected. The following system of equations for the relative populations ρ_a and ρ_b of levels a and b in the $a \rightarrow b$ transition during the short broadband pump pulse is valid under the examined conditions [1]:

$$\rho_a + \rho_b = 1\ , \qquad \frac{d\rho_a}{dt} = \theta(t)(\rho_b - \rho_a)\ , \qquad \frac{d\rho_b}{dt} = \theta(t)(\rho_a - \rho_b)\ , \tag{2}$$

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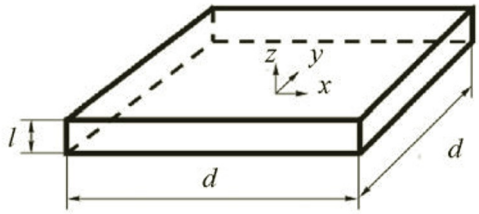

Fig. 1. Thin gas cell in the shape of a rectangular parallelepiped.

where $\theta(t)$ is the rate of optical excitation, which is assumed to be uniform throughout the whole cell volume. The relative populations of levels a and b in the equilibrium state before irradiation of the gas medium are $\rho_a = 1$ and $\rho_b = 0$. Then, we obtain from system of Eqs. (2) for the population of excited level b at the end of the pump pulse $t = 0$:

$$\rho_b^{(0)} = 0.5 \left\{ 1 - \exp \left[-2 \int_0^T \theta(t_1) dt_1 \right] \right\} . \tag{3}$$

The population change ρ_b of level b during time $t > 0$ obeys the equation for atoms with velocity $\mathbf{v}$ and coordinate vector $\mathbf{r}$ [1]:

$$\frac{d\rho_b}{dt} + \mathbf{v} \frac{d\rho_b}{d\mathbf{r}} + \frac{\rho_b}{\tau_b} = 0 . \tag{4}$$

Equation (4) should be constrained by the initial condition $\rho_b(t = 0) = \rho_b^{(0)}$ and boundary conditions that depend on the collisions of atoms (molecules) with the cell walls. Equilibrium distributions both over atomic velocities and the populations of their quantum levels were considered established because of such collisions for thin gas cells, as before [2, 3]. Then, atoms excited to level b relax into ground quantum state a during any collision with the inner surface of the cell. Equation (4) under these conditions gives the relative population $\rho_b(\mathbf{r}, \mathbf{v}, t)$ of excited atoms for a gas cell limited by six walls with coordinates $z = \pm 0.5l$, $x = \pm 0.5d$, and $y = \pm 0.5d$:

$$\rho_b(\mathbf{r}, \mathbf{v}, t) = \rho_b^{(0)} \exp(-t/\tau_b) \eta(0.5l - |z|) \eta(0.5d - |x|) \eta(0.5d - |y|)$$

$$\times \sum_{\alpha=\pm1} \sum_{\beta=\pm1} \sum_{\sigma=\pm1} \left\{ \eta(\alpha v_x) \eta(\beta v_y) \eta(\sigma v_z) \eta[0.5d + \alpha(x - v_x t)] \eta[0.5d + \beta(y - v_y t)] \times \eta[0.5l + \sigma(z - v_z t)] \right\} , \tag{5}$$

where $\eta(p)$ is a step function [$\eta(p) = 1$ for $p \geq 0$ and $\eta(p) = 0$ for $p < 0$]. Let us examine the change dynamics of distribution $N_b(v_z, t)$ of excited atoms along the projection of the atomic velocity v_z in volume V of the gas cell:

$$N_b(v_z, t) = n_a F(v_z) \int_{-\infty}^{+\infty} \int \left[\int \rho_b(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} \right] F(v_x) F(v_y) dv_x dv_y , \tag{6}$$

where n_a is the equilibrium density of atoms in ground state a; $F(v_j)$, the Maxwell distribution along the projection of velocity v_j:

$$F(v_j) = \pi^{-0.5} u^{-1} \exp(-v_j^2/u^2), \; j = x, y, z , \tag{7}$$

with the most probable velocity u of gaseous atoms. By substituting Eq. (5) into Eq. (6), we obtain

$$N_b(v_z, t) = N_0 \rho_b^{(0)} F(v_z) \exp(-t/\tau_b) s(t) (1 - |v_z| \, tl^{-1}) \eta(1 - |v_z| \, tl^{-1}) , \tag{8}$$

where $N_b = n_a V$ is the number of atoms in cell volume $V = ld^2$. The function

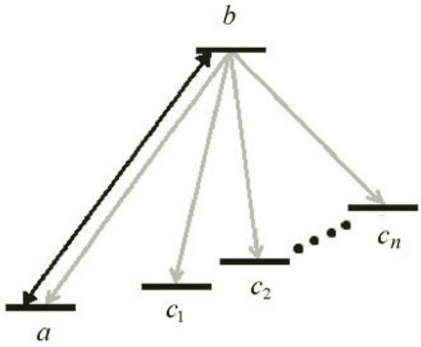

Fig. 2. Diagram of quantum levels and atomic (molecular) transitions: $a \rightarrow b$, transition with excitation from ground term a to level b by pulsed radiation; $b \rightarrow a$, $b \rightarrow c_1$, $b \rightarrow c_2$, …, $b \rightarrow c_n$, spontaneous transitions from excited state b to lower levels a, c_1, c_2, …, c_n.

$$s(t) = 4\left[\int_0^{d/t} F(v)(1 - vtd^{-1}dv\right]^2 , \; t \geq 0 , \tag{9}$$

with function $F(v)$ [Eq. (7)] also describes the decrease in the number of excited atoms over time $t \geq 0$ resulting from collisions with the cell side walls with coordinates $x = \pm 0.5d$ and $y = \pm 0.5d$. The function of Eq. (9) decreases smoothly starting from $s(0) = 1$ with $s(t) \approx \pi^{-1}d^2u^{-2}t^{-2}$, where $t > 2d/u$.

The factor $\exp(-t/\tau_b)$ in Eqs. (5) and (8) describes the decrease in the number of excited particles resulting from their radiative decay from level b into lower-energy quantum states a, c_1, c_2, …, c_n (Fig. 2) after irradiation by the short light pulse. The corresponding fluorescence signal of the gas medium in the cell can be recorded experimentally starting from a certain time point $t > 0$. Therefore, let us analyze the total number $N_b^{(f)}(v_z, t)$ of atomic particles in level b for which radiative decay occurs before their collisions with the cell walls from time $t > 0$:

$$N_b^{(f)}(v_z, t) = \frac{1}{\tau_b}\int_t^{\infty} N_b(v_z, t_1)dt_1 , \tag{10}$$

where the function $N_b(v_z, t)$ is described by Eq. (8). Velocity distribution $N_b^{(f)}(v_z, t)$ determines the Doppler structure of the fluorescence spectral lines from excited level b of gaseous atoms in the direction of the z axis of the thin cell.

Results and Biscussion. Figure 3 shows the calculated dependences of the number $N_b(v_z, t)$ [Eq. (8)] of excited atoms not colliding with the walls of the thin cell by time $t > 0$ after irradiation by the light pulse and the fractions of these atoms $N_b^{(f)}(v_z, -)$ [Eq. (10)] that contribute to the recorded fluorescence of the gas layer starting from time t from the projection of the atomic velocity v_z. According to Eq. (8), the characteristic width $w(t)$ of the velocity distribution $N_b(v_z, t)$ at its half-height is written:

$$w(t) = 2l/t . \tag{11}$$

The decrease of the amplitude $A(t) = N_b(v_z = 0, t)$ of distribution $N_b(v_z, t)$ [Eq. (8)] at time t obeys the following expression for $t > 2d/u$:

$$A(t) \approx \pi^{-1.5}N_0\rho_b^{(0)} \exp(-t / \tau_b)d^2u^{-3}t^{-2} . \tag{12}$$

The probability of radiative decay of excited atomic level b increases with time. Therefore, the relative fraction of excited atoms remaining in the cell that subsequently decay radiatively before colliding with the cell walls increases with time.

Figure 4 shows dependences for amplitude $A_f(t)$ and width $w_f(t)$ of velocity distribution $N_b^{(f)}(v_z, t)$ [Eq. (10)] of fluorescing atoms from time $t > 0$ for various ratios $d/l >> 1$ of the cell transverse dimension d to its fixed inner

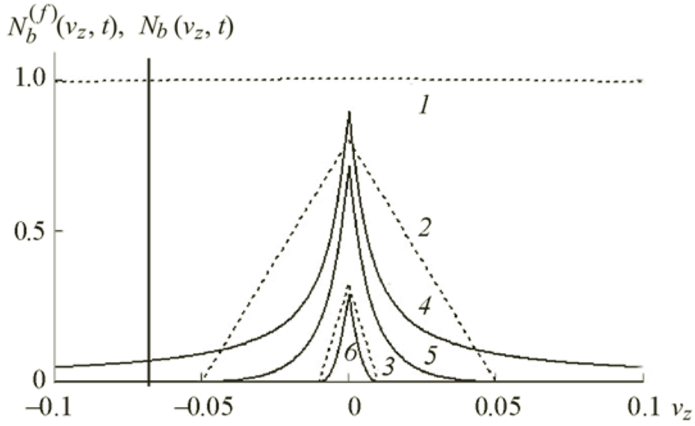

Fig. 3. Dependences of number of excited atoms $N_b(v_z, t)$ (1–3) and their fluorescing fraction $N_b^{(f)}(v_z, t)$ (4–6) on projection of atomic velocity v_z (in units of u) for time points $t = 0$ (1, 4), $0.2\tau_b$ (2, 5), and τ_b (3, 6) for $\tau_b = 100l/u$ and $d/l = 1000$; functions $N_b(v_z, t)$ and $N_b^{(f)}(v_z, t)$ are normalized to $A_0 = N_b$ ($v_z = 0$, $t = 0$).

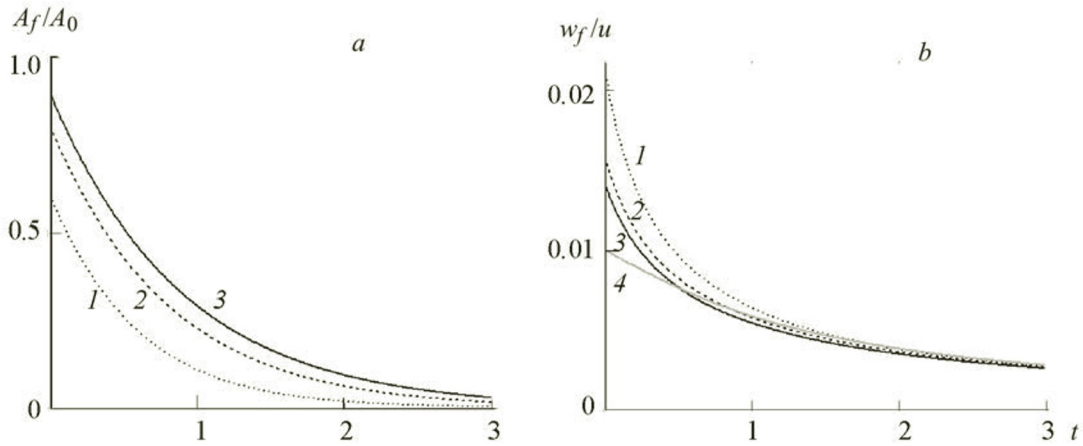

Fig. 4. Dependences of amplitude A_f (a) and width w_f (b) of velocity distribution $N_b^{(f)}(v_z, t)$ of fluorescing atoms on time t (in units of τ_b) for $\tau_b = 100l/u$ and $d/l = 200$ (1), 500 (2), and 1000 (3); approximate dependence $w_f(t)$ described by Eq. (14) (4).

thickness l. The following expressions in addition to Eq. (1) are fulfilled for effective fluorescence of atoms remaining in the cell in excited state b by time $t > 0$:

$$|v_x|\ \tau_b \le d, |v_y|\ \tau_b \le d, |v_z|\ \tau_b \le l\ . \tag{13}$$

According to Eq. (13), a decrease of cell transverse dimension d with its given inner thickness l leads to a decrease of the fraction of fluorescing gaseous atoms. Therefore, the amplitude decreases and velocity distribution $N_b^{(f)}(v_z, t)$ [Eq. (10)] of such atoms broadens as the ratio d/l decreases (Fig. 4). The difference of widths $w_f(t)$ obtained at various ratios $d/l >> 1$ disappears asymptotically with increasing t (Fig. 4b). The function $w_f(t)$ for $t > \tau_b$ obeys well the expression:

$$w_f(t) \approx l\left(t^{-1} + \tau_b^{-1} - \sqrt{t^{-2} + \tau_b^{-2}}\right). \tag{14}$$

Width $w_f(t)$ can formally reach a value as small as suitable at $t > 0$. However, the amplitude $A_f(t)$ of velocity distribution $N_b^{(f)}(v_z, t)$ [Eq. (10)] of fluorescing atoms decreases faster than its width $w_f(t)$ when $t > \tau_b$ and $t > 2d/u$.

According to Fig. 3, the fluorescence spectrum of gaseous atoms recorded in the direction of the thin-cell z axis contains comparatively narrow sub-Doppler resonances with centers at the frequencies of each spontaneous transition from excited level b (Fig. 2). The amplitude and width of such resonances are determined by the corresponding characteristic velocity distribution $N_b^{(f)}(v_z, t)$ [Eq. (10)] of fluorescing atoms that depend considerably on time t of the start of recording and the thin-cell dimensions (Fig. 4). The Doppler broadening of such fluorescence resonances over time disappears asymptotically (Fig. 4b) although the amplitude signal decreases faster (Fig. 4a).

A fluorescence signal was recorded without the exciting radiation in the examined case, in contrast to the sub-Doppler fluorescence resonances with steady-state optical pumping in the thin gas cells [3]. This allowed the accuracy of the experimental measurements to be increased. Such measurements should be based on well-developed spectroscopic techniques with high temporal and spectral resolution [1]. The rather short controlled light pulses (with up to femtosecond duration) required for such experiments could be produced by using lasers that are widely used in spectroscopy.

Conclusions. A gas cell shaped as a rectangular parallelepiped, the geometry of which considerably simplified the theoretical calculations, was examined. The obtained qualitative results could be generalized for thin cells of another shape, particularly for a cylindrical cell of diameter d and inner thickness $l << d$. Currently, ultra-thin gas cells with characteristic dimensions $l \sim 10$ nm and $d \sim 1$ cm with a small ratio $l/d \sim 10^{-6}$ are being fabricated and used in spectroscopy [4]. The examined fluorescence signal of optically excited atoms could be enhanced by using a series of sequentially positioned thin gas cells.

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